Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

How an Early or Late Transition State Impacts the Stereoselectivity of Tetrahydropyran Formation by Intramolecular oxa-Michael Addition

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Supporting Information III: Details of computational studies
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acid-catalysed *oxa*-Michael cyclisation

10b-protonated

E(wb97xd/6-311++G(3df,3pd)/SMD(MeOH)) = -3460.534882
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(MeOH)) = 0.370124
1 1

C	-0.30963600	-1.31419500	-0.12995900
C	-0.58010000	-0.57509200	-1.43716100
C	-0.20124000	-1.38314200	-2.67835900
C	-0.81855100	-0.53127900	1.07198800
H	-1.64489900	-0.32887700	-1.51127800
H	-0.79442700	-2.29708200	-0.15904900
H	0.76522300	-1.49295000	-0.02245800
H	-1.89695800	-0.33580600	0.98714600
H	-0.36791000	0.47181100	1.10607100
H	-0.80617100	-2.29343500	-2.70377000
O	-0.56232800	-0.67349700	-3.86614200
C	-0.60049500	-1.13131400	2.40490300
H	-1.00118900	-0.56961300	3.24516700
C	0.04195500	-2.29680400	2.64782900
H	0.45572400	-2.88836500	1.84309100
C	0.21426300	-2.78946300	3.97177300
O	-0.15831900	-2.02512400	4.94548000
H	-0.02560200	0.37223000	-1.44840600
C	3.95721800	-2.53860000	-2.61965000
C	2.96150200	-3.49823700	-2.47766500
C	1.62111200	-3.12215500	-2.51254700
C	1.26059100	-1.78737500	-2.68388100
C	2.26745600	-0.82973200	-2.82199900
C	3.60600300	-1.20190900	-2.79439200
H	5.00225500	-2.82867000	-2.59668000
H	3.22601400	-4.54195400	-2.34388700
H	0.84598800	-3.87518600	-2.40406200
H	2.00637400	0.21662800	-2.95321700
H	4.37806300	-0.44795000	-2.90687500
H	-0.19995500	0.21682900	-3.82020800
C	0.81018300	-4.09208500	4.24016800
C	1.49895900	-4.32309100	5.43912600
C	0.69603900	-5.12212800	3.29742600
C	2.06649900	-5.55833900	5.69244400
H	1.63628300	-3.53072100	6.16745000
C	1.24258300	-6.36694200	3.55456600
H	0.15130500	-4.97121300	2.37392500
C	1.92619500	-6.57028500	4.74829700
H	2.61415400	-5.72260400	6.61162300
H	1.13339700	-7.16365700	2.82971400
Br	2.69149500	-8.26873300	5.09732900
H	-0.11500200	-2.44604400	5.81698900

Transition state 1.1-trans

E(wb97xd/6-311++G(3df,3pd)/SMD(MeOH)) = -3460.526603
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(MeOH)) = 0.369429
Imaginary frequency: 233.48i

1 1

C	1.09330700	-1.62008800	-3.51345000
C	2.19844300	-0.77847200	-4.06221800
H	3.15777100	-1.19719200	-3.75086100
H	2.13752000	-0.88507800	-5.15260200
C	2.11381000	0.70152200	-3.67598900
H	1.16493300	1.13065300	-4.01309300
C	2.27965700	0.92964100	-2.17357900
H	2.18910300	1.99576500	-1.94897300
H	3.27839000	0.61249600	-1.85290800
C	1.24317500	0.19137100	-1.33849700
H	0.23476800	0.47104600	-1.66192400
O	1.42567900	-1.22142300	-1.62224200
H	0.76503200	-1.73445900	-1.13805700
H	2.90468300	1.23770100	-4.20572800
C	1.37388700	0.42984100	0.14474000
C	0.37190600	1.11206500	0.83089700
C	2.50222800	-0.00933600	0.84038600
C	0.49685400	1.36299600	2.19441000
H	-0.51049500	1.44950200	0.29558500
C	2.62379100	0.23376800	2.20266400
H	3.28536200	-0.54673300	0.31543300
C	1.62216400	0.92316500	2.88222200
H	-0.28833000	1.89669100	2.71900800
H	3.50244100	-0.11302900	2.73600200
H	1.71934900	1.11400200	3.94562200
H	1.33012200	-2.66006800	-3.31813700
C	-0.25700700	-1.30128500	-3.77019600
H	-0.50693300	-0.36321300	-4.24627200
C	-1.27720600	-2.15387600	-3.44290900
O	-0.99207800	-3.30417600	-2.85135600
H	-1.78576200	-3.78349100	-2.58142300
C	-2.69069900	-1.84447600	-3.73133200
C	-3.56674400	-2.85952700	-4.12542200
C	-3.16315600	-0.53535000	-3.61388800
C	-4.89490800	-2.57402000	-4.40368700
H	-3.21537100	-3.87885500	-4.24728000
C	-4.49196400	-0.24182200	-3.87972900
H	-2.50168900	0.25970100	-3.29007500
C	-5.34404500	-1.26608300	-4.27373100
H	-5.56175800	-3.36618000	-4.72057000
H	-4.85201900	0.77399400	-3.77351700
Br	-7.16646500	-0.86830400	-4.64023000

Transition state 1.1-cis

E(wb97xd/6-311++G(3df,3pd)/SMD(MeOH)) = -3460.527746
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(MeOH)) = 0.369441
Imaginary frequency: 215.10i
1 1

C	0.37561600	-4.07536700	-2.73617600
O	-0.83124800	-3.65882300	-2.38069100
C	1.30955400	-3.15840700	-3.13874600
C	1.03563700	-1.77639900	-3.16807200
C	1.91600100	-0.83935200	-3.91451400
H	2.96271000	-1.12919600	-3.78065600
H	1.67331000	-1.01667600	-4.97137500
H	2.28386200	-3.51105400	-3.45070400
H	0.00083900	-1.46667700	-3.05010400
C	1.69351200	0.63482500	-3.58052300
H	0.64508800	0.89463600	-3.76624300
C	2.06259800	0.99043800	-2.14203800
H	1.90588600	2.05902100	-1.97212200
H	3.12349200	0.78386700	-1.96075500
C	1.23292500	0.23566000	-1.11537400
H	0.16834200	0.42120100	-1.28952700
O	1.48209000	-1.17755100	-1.35376800
H	0.91734300	-1.70842700	-0.77566000
H	-1.37237700	-4.37212800	-2.01974600
H	2.29645500	1.23931000	-4.26232500
C	1.57998600	0.58232400	0.31082700
C	0.66624100	1.27576600	1.10111700
C	2.82372700	0.23905500	0.84458600
C	0.99168200	1.63195900	2.40688100
H	-0.30447200	1.54055900	0.69303600
C	3.14557100	0.58648700	2.15054400
H	3.54011300	-0.30500200	0.23761000
C	2.23089700	1.28651700	2.93396500
H	0.27367900	2.17410400	3.01285200
H	4.11290100	0.31318900	2.55840300
H	2.48436900	1.55906100	3.95284400
C	0.65284700	-5.52419500	-2.70868300
C	1.91183200	-5.99242700	-2.32595300
C	-0.33877900	-6.43717200	-3.07646400
C	2.17864500	-7.35286600	-2.30589000
H	2.68524000	-5.29829800	-2.01908300
C	-0.07763100	-7.79921300	-3.07187700
H	-1.31644000	-6.09402600	-3.39775700
C	1.18028300	-8.24214600	-2.68377700
H	3.15338200	-7.70754600	-1.99476600
H	-0.84835500	-8.49774600	-3.37305400
Br	1.54480500	-10.10770600	-2.66893400

Enol 1.2-trans

E(wb97xd/6-311++G(3df,3pd)/SMD(MeOH)) = -3460.530372
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(MeOH)) = 0.371799
1 1

C	1.11829000	-1.41462900	-3.44258700
C	2.14645500	-0.55758100	-4.15249400
H	3.13804500	-0.97894900	-3.96553300
H	1.94840500	-0.64361300	-5.22400300
C	2.11159100	0.90376800	-3.70497300
H	1.16052700	1.36837300	-3.98358100
C	2.31837800	1.02047100	-2.19550300
H	2.21710800	2.05840000	-1.86856700
H	3.32322800	0.68418700	-1.92177600
C	1.29231100	0.21413700	-1.42618100
H	0.27729200	0.52580500	-1.67955600
O	1.42000000	-1.19645600	-1.92993800
H	0.87111700	-1.79696300	-1.39712000
H	2.89850300	1.45528200	-4.22362900
C	1.46775200	0.16817800	0.06277400
C	0.42616300	0.59300000	0.88517200
C	2.65835200	-0.28515800	0.63460700
C	0.57637500	0.58172800	2.26806400
H	-0.50252800	0.93775800	0.44172000
C	2.80219200	-0.30709800	2.01555200
H	3.47070900	-0.62616700	0.00145500
C	1.76336000	0.13032500	2.83369700
H	-0.23608900	0.91983800	2.90173800
H	3.72717400	-0.66349800	2.45535500
H	1.88016600	0.11655100	3.91195900
H	1.35180600	-2.47335900	-3.52529500
C	-0.29861100	-1.10739500	-3.73145800
H	-0.55734700	-0.11420100	-4.08236800
C	-1.28580300	-1.99418800	-3.54258000
O	-2.56143300	-1.61039900	-3.77775400
H	-3.16474400	-2.35518700	-3.67877000
C	-1.09523800	-3.38630200	-3.05306600
C	-0.58309900	-4.37158200	-3.89473900
C	-1.43228900	-3.70645600	-1.73825300
C	-0.40153700	-5.66802600	-3.42967400
H	-0.32124300	-4.12735300	-4.91822100
C	-1.25255800	-4.99824700	-1.26122400
H	-1.82937100	-2.94333100	-1.07750700
C	-0.73700600	-5.96447000	-2.11532000
H	-0.00260800	-6.42873200	-4.08954400
H	-1.50889400	-5.23824500	-0.23668300
Br	-0.48312200	-7.73673500	-1.46669400

Enol 1.2-cis

E(wb97xd/6-311++G(3df,3pd)/SMD(MeOH)) = -3460.533869
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(MeOH)) = 0.371435
1 1

C	0.36569600	-4.02441700	-2.64280900
O	-0.91093500	-3.62800800	-2.43830000
C	1.32093400	-3.10852100	-2.87629200
C	1.06177800	-1.65701700	-2.87227600
C	1.87458200	-0.84824300	-3.85553400
H	2.93092300	-1.11720100	-3.75042200
H	1.55429300	-1.15759000	-4.85413700
H	2.32694200	-3.44294800	-3.09690500
H	0.00019000	-1.41234700	-2.91892900
C	1.67809300	0.65336800	-3.66471100
H	0.63469900	0.91653100	-3.87066700
C	2.04384300	1.07776000	-2.24445600
H	1.83716900	2.13974800	-2.08901000
H	3.11106100	0.91902400	-2.06158900
C	1.24010400	0.32024600	-1.20799200
H	0.16788500	0.46002500	-1.36181300
O	1.48953200	-1.14116800	-1.47716400
H	1.07275200	-1.68962700	-0.79043300
H	-1.45699200	-4.35355700	-2.11666300
H	2.29747400	1.19853400	-4.38004100
C	1.61233300	0.57741000	0.22222500
C	0.64764700	1.05955100	1.10443400
C	2.91429200	0.35556600	0.67605300
C	0.98264100	1.33400100	2.42650000
H	-0.36625800	1.22504200	0.75436500
C	3.24353500	0.61754900	1.99919600
H	3.66856400	-0.02829400	-0.00280900
C	2.27951400	1.11153900	2.87481500
H	0.22863800	1.71598900	3.10585900
H	4.25486200	0.43999200	2.34810200
H	2.54059700	1.32048900	3.90661600
C	0.63907400	-5.48145600	-2.63803100
C	1.80379000	-5.97927600	-2.05166300
C	-0.26240900	-6.37184000	-3.22489400
C	2.07162700	-7.34102600	-2.05491800
H	2.50302700	-5.30380700	-1.57246900
C	-0.00465200	-7.73585000	-3.23680900
H	-1.16826900	-6.00595500	-3.69636800
C	1.16253100	-8.20599600	-2.65006100
H	2.97527600	-7.71514000	-1.58944400
H	-0.70752000	-8.41486000	-3.70363000
Br	1.52029200	-10.07564000	-2.65562000

THP 1.3-trans

E(wb97xd/6-311++G(3df,3pd)/SMD(MeOH)) = -3460.546513
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(MeOH)) = 0.372284
1 1

C	-0.01322300	0.01073600	0.03752600
C	0.91176600	0.93145200	-0.75346600
H	1.93861400	0.60545900	-0.55759100
H	0.72375800	0.79633700	-1.82211900
C	0.76207200	2.39488800	-0.34025300
H	-0.20797500	2.78735000	-0.66604300
C	0.88016500	2.52215600	1.17731800
H	0.69026400	3.54940300	1.50139700
H	1.89145900	2.25141100	1.50250100
C	-0.12459200	1.59960000	1.86100900
H	-1.13649100	1.91611700	1.57967700
O	0.07412600	0.23896300	1.43944500
H	1.52862200	2.99719000	-0.83433600
C	-0.02537300	1.61139700	3.36475300
C	-1.04137300	2.17790200	4.13104400
C	1.09083900	1.07308900	4.00807100
C	-0.94475800	2.21406200	5.51971100
H	-1.91575400	2.59316600	3.63869100
C	1.18546200	1.10093700	5.39406800
H	1.88722800	0.62653300	3.42167000
C	0.16808000	1.67367900	6.15394800
H	-1.74252400	2.65928400	6.10479900
H	2.05560200	0.67646100	5.88373800
H	0.24367400	1.69623200	7.23590300
H	0.30891200	-1.02419500	-0.08725600
C	-1.48630100	0.10882100	-0.44513400
H	-1.54792800	-0.33746300	-1.44021700
C	-2.36543600	-0.61917400	0.49659700
O	-3.12935700	0.13861700	1.18544400
H	-3.72325700	-0.32213600	1.80046400
C	-2.33059000	-2.05117200	0.68864200
C	-1.80614600	-2.87284700	-0.32164200
C	-2.78726500	-2.63198900	1.88493500
C	-1.76193600	-4.24439800	-0.15584400
H	-1.45521900	-2.45259000	-1.25526100
C	-2.72869100	-3.99956900	2.06279100
H	-3.14948900	-2.02827900	2.70992100
C	-2.22318900	-4.79301900	1.03588700
H	-1.37078600	-4.87113900	-0.94708400
H	-3.06580300	-4.43735300	2.99357000
Br	-2.15412200	-6.66886500	1.27450700
H	-1.82884000	1.14119300	-0.50470400

THP 1.3-cis

E(wb97xd/6-311++G(3df,3pd)/SMD(MeOH)) = -3460.546828
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(MeOH)) = 0.371155
1 1

C	-0.43292100	0.02803100	0.05365100
O	-1.44562100	0.59309300	0.58336500
C	0.52684000	0.94324600	-0.61200500
C	0.24460500	2.42725300	-0.46334100
C	1.14653000	3.25639000	-1.36977200
H	2.19052000	2.98154300	-1.17687700
H	0.92521900	3.01501000	-2.41350400
H	1.52999500	0.72285400	-0.23106400
H	-0.80487700	2.63867400	-0.71095900
C	0.93552700	4.74449400	-1.09821800
H	-0.07079800	5.03379800	-1.42482900
C	1.08772100	5.03781300	0.39292800
H	0.83040300	6.07713500	0.61682200
H	2.12649800	4.87823800	0.70557500
C	0.18633900	4.11644800	1.21533800
H	-0.86257200	4.31939300	0.95584900
O	0.46542000	2.74773300	0.90730100
H	-2.06477200	-0.00262700	1.03482000
H	1.64501800	5.34076400	-1.67789300
C	0.36980900	4.30765500	2.69933800
C	-0.55610700	5.05059400	3.42891800
C	1.48841300	3.78787500	3.35307900
C	-0.36927800	5.27545600	4.78989800
H	-1.43094000	5.45592700	2.92907000
C	1.67191300	4.00398700	4.71397000
H	2.21779000	3.20960700	2.79566000
C	0.74459200	4.75070300	5.43622300
H	-1.09829700	5.85582300	5.34555200
H	2.54295400	3.59128600	5.21216000
H	0.88989400	4.92076200	6.49772700
C	-0.25228800	-1.40778000	0.07353600
C	0.94723400	-1.96190500	-0.40280200
C	-1.26191100	-2.26404000	0.54481800
C	1.14179300	-3.32983800	-0.39487300
H	1.74359900	-1.33218000	-0.77661400
C	-1.07695600	-3.63181700	0.55143200
H	-2.21844600	-1.89301400	0.89583300
C	0.12727200	-4.15166800	0.08419100
H	2.07366100	-3.74400800	-0.75772700
H	-1.86464500	-4.28028500	0.91273600
Br	0.38608300	-6.02554200	0.09602900
H	0.54004700	0.66341300	-1.67242500

base-catalysed *oxa*-Michael cyclisation (*E*-alkene)

10a-alkoxide

E(wb97xd/6-311++G(3df,3pd)/SMD(THF)) = -769.4970173
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(THF)) = 0.290949
-1 1

C	-0.34026000	-1.33221700	0.01756000
C	-0.60492000	-0.63980900	-1.31800900
C	-0.34877900	-1.47428000	-2.61176200
C	-0.76951800	-0.48524800	1.21052100
H	-1.65681000	-0.33133800	-1.36825700
H	-0.87476700	-2.29079600	0.04278300
H	0.72535300	-1.57019300	0.10902400
H	-1.83773500	-0.24056800	1.13343300
H	-0.25879900	0.48726300	1.18238200
H	-0.91159300	-2.43443200	-2.44211600
O	-0.72782700	-0.81674800	-3.72233600
C	-0.54099800	-1.07177500	2.56490400
H	-0.86149000	-0.46388600	3.40958600
C	0.01202100	-2.25670300	2.83100500
H	0.36016000	-2.92282500	2.05000200
C	0.17784100	-2.72003800	4.22145600
O	-0.14953700	-2.12021100	5.22146700
O	0.75498200	-3.93056800	4.25609400
C	0.97179100	-4.49585200	5.55117900
H	0.02464700	-4.63271300	6.07672500
H	1.44452200	-5.46067200	5.37588500
H	1.62949500	-3.85911200	6.14606700
H	-0.00322700	0.27706300	-1.39021600
C	3.86350000	-2.59563600	-2.61812200
C	2.92090600	-3.45325300	-2.05966000
C	1.57164900	-3.10408300	-2.06126800
C	1.13377600	-1.90131700	-2.61804700
C	2.09053900	-1.05824700	-3.18644300
C	3.44006500	-1.39368500	-3.18348900
H	4.91522200	-2.86367800	-2.62170000
H	3.23571100	-4.39789000	-1.62609700
H	0.84209200	-3.78243900	-1.62492600
H	1.74366000	-0.13951000	-3.64877300
H	4.16687900	-0.72114700	-3.62986100

Transition state 2.1-cis

E(wb97xd/6-311++G(3df,3pd)/SMD(THF)) = -769.4903492
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(THF)) = 0,289828
Imaginary frequency: 63.64i
-1 1

C	-3.60875300	-0.43002800	0.21554200
O	-3.54769100	-0.64308400	1.41279400
C	-2.83338800	0.52372200	-0.55184800
C	-1.82932300	1.23024600	0.01297300
C	-1.14964100	2.37523200	-0.67315700
H	-0.99392500	2.12711900	-1.72842000
H	-1.86212700	3.21311300	-0.65673500
H	-3.04780000	0.59915200	-1.61299300
H	-1.67558100	1.13097600	1.08210600
C	0.15928700	2.85743600	-0.04228900
H	0.00333000	2.99861900	1.03639800
C	1.36909200	1.95185400	-0.25970300
H	1.52896500	1.80331300	-1.33718700
H	2.26250400	2.45469500	0.13479100
C	1.19439000	0.55748600	0.39173700
H	1.13653800	0.76033800	1.49599800
O	0.10642100	-0.08896200	-0.07941400
H	0.38336700	3.85055000	-0.44944900
O	-4.48741900	-1.10226200	-0.57430100
C	-5.31035600	-2.06359600	0.07676300
H	-5.93807200	-1.59556100	0.83925300
H	-5.93757400	-2.49539700	-0.70288100
H	-4.70797500	-2.84734900	0.54222700
C	2.50991700	-0.21941000	0.21222300
C	3.67587200	0.13473400	0.89744500
C	2.56563200	-1.29705200	-0.66862700
C	4.86512400	-0.55918200	0.70028600
H	3.64951700	0.96387500	1.60091100
C	3.75373800	-1.99489500	-0.87505800
H	1.64679200	-1.57320900	-1.17534000
C	4.90981800	-1.62888600	-0.19217500
H	5.75834800	-0.27017300	1.24596300
H	3.77669300	-2.83193900	-1.56675900
H	5.83535600	-2.17414800	-0.34702400

Transition state 2.1-trans

E(wb97xd/6-311++G(3df,3pd)/SMD(THF)) = -769.4913589
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(THF)) = 0.290401
Imaginary frequency: 97.14i
-1 1

C	3.23329100	-0.62314500	0.18457500
O	3.46518800	-0.97367400	1.32610500
C	2.50313200	0.55590200	-0.24882300
C	1.90183100	1.37572500	0.64038800
C	1.26768500	2.68787200	0.27256900
H	0.74178900	3.08060300	1.14484900
H	2.07965100	3.39251700	0.04126900
H	2.42385000	0.71160400	-1.31875900
H	2.05011700	1.17640800	1.69394400
C	0.30447400	2.63940800	-0.92015800
H	0.79888300	2.15530500	-1.77104400
C	-1.02330900	1.93459700	-0.63614600
H	-1.61208900	2.52913900	0.07620300
H	-1.59695100	1.88453400	-1.57127800
C	-0.84722900	0.52577500	-0.00405200
H	-0.22408800	-0.05293200	-0.74113700
O	-0.27596800	0.59126300	1.21411100
H	0.10097700	3.66899500	-1.23762900
C	-2.20791300	-0.19106000	-0.01670000
C	-2.85278400	-0.47822900	1.18404100
C	-2.83479500	-0.56824900	-1.20847100
C	-4.09301000	-1.11352600	1.20050300
H	-2.34343600	-0.19606100	2.09953300
C	-4.07139500	-1.20441600	-1.20117500
H	-2.34148400	-0.36821600	-2.15688800
C	-4.70940000	-1.47851200	0.00777500
H	-4.57839400	-1.32874700	2.14800700
H	-4.53818100	-1.49266900	-2.13831500
H	-5.67336900	-1.97710600	0.01722800
O	3.67831600	-1.34146500	-0.87799300
C	4.41373300	-2.52266600	-0.57666700
H	4.67914600	-2.96119900	-1.53826700
H	5.32062400	-2.28988800	-0.01324100
H	3.80752900	-3.22798700	-0.00347900

enolate 2.2-cis

E(wb97xd/6-311++G(3df,3pd)/SMD(THF)) = -769.5147312
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(THF)) = 0.292495
-1 1

C	-3.28795700	-0.75326000	-0.48161800
O	-4.19404100	-1.35148300	-1.09620200
C	-2.49535400	0.30195300	-0.91391500
C	-1.40991400	0.92213500	-0.12709200
C	-1.23962500	2.41872900	-0.40409000
H	-1.06945400	2.55440400	-1.48010300
H	-2.17490100	2.92994300	-0.15658300
H	-2.63390900	0.61947300	-1.94434900
H	-1.59865200	0.78060700	0.94707500
C	-0.07896600	3.02253500	0.38645700
H	-0.33025500	3.01480100	1.45533600
C	1.19721100	2.21431600	0.16943600
H	1.54538500	2.32425200	-0.86502100
H	2.00005600	2.56235500	0.82748800
C	0.92390300	0.72634500	0.42423700
H	0.63804100	0.60965500	1.48479300
O	-0.12416100	0.26262800	-0.39225300
H	0.07905900	4.06909800	0.10592700
O	-3.01541800	-1.16099200	0.83430000
C	-3.83419700	-2.18653700	1.34640300
H	-3.74900700	-3.11168600	0.76675800
H	-3.48681100	-2.37131400	2.36603200
H	-4.89062800	-1.89782900	1.37552400
C	2.16048100	-0.10769900	0.17660600
C	3.19939900	-0.09893300	1.10952500
C	2.31170300	-0.85507500	-0.98964100
C	4.36809600	-0.81556300	0.88031900
H	3.08893700	0.47202900	2.02729600
C	3.48088200	-1.57519400	-1.22052000
H	1.50116700	-0.87540800	-1.70814700
C	4.51397000	-1.55630300	-0.28973000
H	5.16415200	-0.80032500	1.61764600
H	3.58248000	-2.15544200	-2.13194900
H	5.42373900	-2.11913700	-0.47009200

enolate 2.2-trans

E(wb97xd/6-311++G(3df,3pd)/SMD(THF)) = -769.5137112
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(THF)) = 0.292761
-1 1

C	2.97781500	-0.75259100	0.19503400
O	3.11565900	-1.22409200	1.33939900
C	2.18650400	0.29994300	-0.24453000
C	1.31210500	1.04843500	0.68928200
C	1.15792200	2.53992500	0.35860300
H	0.65837900	3.03801000	1.19920900
H	2.14751800	2.99263200	0.24760600
H	2.21322400	0.55465900	-1.29837900
H	1.70023000	0.93599900	1.70401100
C	0.32037700	2.74907700	-0.90429000
H	0.85729100	2.35737600	-1.77615200
C	-1.02295800	2.03170000	-0.77046500
H	-1.63515400	2.52268200	-0.00298900
H	-1.58243200	2.06699400	-1.71103900
C	-0.80699500	0.57109400	-0.34673700
H	-0.25919600	0.05601300	-1.15193000
O	-0.05411400	0.50752200	0.83744100
H	0.16201800	3.81724700	-1.08584100
C	-2.12341500	-0.14393100	-0.14576700
C	-2.62064100	-0.41609300	1.12718300
C	-2.88455900	-0.51464300	-1.25667000
C	-3.85473800	-1.04152400	1.28664700
H	-2.02608200	-0.14363700	1.99075700
C	-4.11723600	-1.13720200	-1.10042200
H	-2.50223100	-0.32015400	-2.25483000
C	-4.60872700	-1.40244800	0.17537800
H	-4.22564100	-1.25061600	2.28496500
H	-4.69239100	-1.42269200	-1.97522900
H	-5.56853000	-1.89253700	0.30035000
O	3.73017800	-1.33107000	-0.84662200
C	4.59160700	-2.38142900	-0.47418200
H	5.08146700	-2.71347400	-1.39302200
H	5.35663000	-2.05667000	0.24004000
H	4.05003600	-3.22510900	-0.03293200

Transition state 3.1-cis

E(wb97xd/6-311++G(3df,3pd)/SMD(THF)) = -769.4899223
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(THF)) = 0.290169
Imaginary frequency: 56.65i
-1 1

C	-3.64604000	-0.61022500	-0.41902800
O	-4.41071900	-1.24153800	-1.13396000
C	-2.84510200	0.51172400	-0.85123600
C	-1.91716000	1.13530600	-0.08168500
C	-1.27485300	2.42581900	-0.49470600
H	-1.04370300	2.38996900	-1.56493200
H	-2.03794500	3.20796900	-0.37108700
H	-2.97094100	0.78083500	-1.89567100
H	-1.85076300	0.86913600	0.96647600
C	-0.03569600	2.84337200	0.30037500
H	-0.26894200	2.79773800	1.37347100
C	1.22091500	2.02193600	0.02526000
H	1.46005200	2.06237200	-1.04688300
H	2.06575700	2.47018300	0.56491100
C	1.04720600	0.53537900	0.41886100
H	0.90895600	0.54352800	1.53356800
O	0.00905400	-0.04033300	-0.23130600
H	0.17078000	3.89686600	0.07788300
O	-3.50547100	-0.91871700	0.89307800
C	-4.24358200	-2.04067000	1.35943900
H	-3.96108400	-2.95012400	0.82356800
H	-3.99129000	-2.14368000	2.41472200
H	-5.31954500	-1.88210200	1.25081200
C	2.38700600	-0.18390200	0.19825400
C	3.50757500	0.08396400	0.99022900
C	2.51285000	-1.11725200	-0.82790300
C	4.72142700	-0.55360500	0.75662700
H	3.42582500	0.79812200	1.80637300
C	3.72602600	-1.75814200	-1.07000800
H	1.62739100	-1.32853400	-1.41848200
C	4.83706000	-1.47758800	-0.28047800
H	5.57889200	-0.33379400	1.38551900
H	3.80416900	-2.48222600	-1.87565300
H	5.78240900	-1.97778600	-0.46473100

Transition state 3.1-trans

E(wb97xd/6-311++G(3df,3pd)/SMD(THF)) = -769.490731
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(THF)) = 0.290558
Imaginary frequency: 78.11i
-1 1

C	-3.21479500	-0.62182500	0.60357800
O	-3.62596100	-1.11838700	1.64188500
C	-2.46945600	0.61535000	0.51894200
C	-1.94141200	1.12240600	-0.62594700
C	-1.34883900	2.50416300	-0.70692800
H	-0.91855600	2.64653400	-1.70058000
H	-2.17267400	3.22516700	-0.60607500
H	-2.30254000	1.09431000	1.47771500
H	-2.18971500	0.64265600	-1.56238900
C	-0.28665000	2.81897600	0.35329300
H	-0.69212400	2.61537600	1.35168100
C	1.02345500	2.05224400	0.17094900
H	1.53247500	2.40049600	-0.73865500
H	1.68400400	2.27373000	1.01962200
C	0.80821200	0.52296400	0.01187800
H	0.29218500	0.19407000	0.95292600
O	0.08760800	0.23194700	-1.09362700
H	-0.08091500	3.89550700	0.32571900
C	2.17655600	-0.16863300	0.05541500
C	2.70559200	-0.74313800	-1.09799700
C	2.93300200	-0.22798600	1.22970600
C	3.95934400	-1.35130200	-1.08711100
H	2.09869900	-0.70860300	-1.99649500
C	4.18390500	-0.83521800	1.24957500
H	2.53055700	0.20094900	2.14444700
C	4.70553100	-1.39897600	0.08625800
H	4.35379900	-1.79390300	-1.99709200
H	4.75222200	-0.87534600	2.17391600
H	5.68022100	-1.87611300	0.09870300
O	-3.45815800	-1.20780700	-0.59238500
C	-4.17295400	-2.43659600	-0.56018800
H	-4.26218500	-2.75436200	-1.59884700
H	-3.63113900	-3.19419700	0.01110400
H	-5.16785700	-2.30578500	-0.12709100

Chelated transition state 3.2-cis

E(wb97xd/6-311++G(3df,3pd)/SMD(THF)) = -1369.394217
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(THF)) = 0,293018
Imaginary frequency: 107.89i
0 1

C	-3.36204600	-0.18113900	-0.00779100
O	-3.02540500	-0.85613400	0.96845600
C	-2.66611300	0.94821200	-0.54918300
C	-1.60646400	1.51596600	0.10211700
C	-1.01327400	2.81422000	-0.35845700
H	-0.92117500	2.79633200	-1.44949400
H	-1.74927900	3.59509900	-0.12306200
H	-2.98251600	1.31413700	-1.51975200
H	-1.44075000	1.24579700	1.14073400
C	0.32095400	3.20417000	0.28041700
H	0.20737900	3.20385800	1.37301300
C	1.50094100	2.31297400	-0.09925600
H	1.64994600	2.32937800	-1.18690900
H	2.41444800	2.70588000	0.36334800
C	1.27049400	0.85316200	0.32724100
H	1.16483300	0.87895900	1.43931900
O	0.15224500	0.33084200	-0.27505600
H	0.54503200	4.23794300	-0.00372100
O	-4.47887000	-0.48836200	-0.70081900
C	-5.22311200	-1.61783300	-0.25048400
H	-5.58810700	-1.46798600	0.76780600
H	-6.06527200	-1.70736600	-0.93536300
H	-4.61956200	-2.52793700	-0.28621400
C	2.52316500	0.01746800	0.05906900
C	3.64534400	0.11208400	0.88623800
C	2.57063100	-0.85563900	-1.02646800
C	4.78681000	-0.63972000	0.63185700
H	3.62164600	0.78125700	1.74264700
C	3.71238400	-1.61060400	-1.28711500
H	1.69578700	-0.92781900	-1.66435200
C	4.82459200	-1.50620600	-0.45867300
H	5.64762600	-0.55505300	1.28747300
H	3.73301600	-2.28205700	-2.13988000
H	5.71361800	-2.09521300	-0.65795600
K	-0.60584300	-1.84633500	0.65423000

Chelated transition state 3.2-trans

E(wb97xd/6-311++G(3df,3pd)/SMD(THF)) = -1369.395348
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(THF)) = 0.293633
Imaginary frequency: 147.45i
0 1

C	-2.98862400	-0.32212700	0.33579600
O	-2.94103500	-1.17562600	-0.55348400
C	-2.35050500	0.96134900	0.32455700
C	-1.69776200	1.40797200	-0.79273900
C	-1.12393400	2.79483200	-0.89747800
H	-0.63335100	2.90274300	-1.86766700
H	-1.96135800	3.50457800	-0.87967600
H	-2.34503600	1.52348900	1.25060900
H	-1.90629200	0.90748100	-1.73095900
C	-0.13448600	3.16014700	0.21548900
H	-0.61544900	3.03131400	1.19225800
C	1.16194800	2.35026100	0.17759900
H	1.73349000	2.60057800	-0.72595100
H	1.78044100	2.62068100	1.04196000
C	0.90070200	0.82990300	0.15417500
H	0.30983500	0.60302500	1.07205600
O	0.21445500	0.46432900	-0.97442700
H	0.10221300	4.22613300	0.13028200
C	2.21440700	0.06872400	0.31219600
C	2.85090700	-0.48892600	-0.79595600
C	2.81670200	-0.07450700	1.56461800
C	4.05878700	-1.16979600	-0.66036800
H	2.38576800	-0.37451600	-1.76973700
C	4.02216100	-0.75263900	1.70660000
H	2.33004000	0.34740200	2.44029900
C	4.64893800	-1.30529000	0.59184500
H	4.54103300	-1.59462800	-1.53528100
H	4.47162900	-0.85690100	2.68900500
H	5.58800300	-1.83754500	0.70064600
O	-3.67758800	-0.55521500	1.47228200
C	-4.31896700	-1.82342600	1.58466900
H	-4.79823000	-1.82552800	2.56279800
H	-5.07098200	-1.95452100	0.80362300
H	-3.59315800	-2.63796900	1.52664100
K	-0.58956000	-1.80497500	-1.53970800

base-catalysed *oxa*-Michael cyclisation (*Z*-alkene)

Transition state 5.1-cis

E(wb97xd/6-311++G(3df,3pd)/SMD(THF)) = -769.488223
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(THF)) = 0.290369
Imaginary frequency: 76.15i

-1 1

C	-2.68657200	0.09008900	1.04585900
C	-1.64678400	0.94494200	0.83430300
C	-1.44073700	1.80720400	-0.37499100
H	-1.54730000	1.20157700	-1.27651900
H	-2.26876000	2.52980100	-0.40347300
H	-1.08332500	1.23495700	1.71541400
C	-0.11589500	2.57307400	-0.39074000
H	0.00133400	3.11101500	0.56075800
C	1.12225300	1.71205500	-0.63454100
H	1.04367700	1.22231200	-1.61511900
H	2.00706700	2.36165700	-0.66444900
C	1.28830100	0.60287300	0.43277200
H	1.41869500	1.15190100	1.40482000
O	0.22854200	-0.24009300	0.45262400
H	-0.17348600	3.34202600	-1.17015700
C	2.63300700	-0.10413800	0.20672600
C	3.85242300	0.55084100	0.40436300
C	2.65904700	-1.43027500	-0.21837700
C	5.06159600	-0.09588100	0.17254100
H	3.85477000	1.58177200	0.75050300
C	3.86637500	-2.08445100	-0.45509100
H	1.70522600	-1.93083300	-0.34776900
C	5.07355600	-1.42028500	-0.26209300
H	5.99735600	0.43045500	0.33484200
H	3.86493400	-3.11852100	-0.78699100
H	6.01533200	-1.92861100	-0.44232100
H	-2.78827600	-0.38243700	2.01620400
C	-3.62717500	-0.33666800	0.03727000
O	-3.71536700	0.02949000	-1.12324100
O	-4.49923000	-1.25600400	0.54284200
C	-5.48843000	-1.74228700	-0.35493100
H	-5.03335900	-2.24612800	-1.21130400
H	-6.08442300	-2.45441000	0.21585200
H	-6.12802300	-0.93332200	-0.71736600

Transition state 5.1-trans

E(wb97xd/6-311++G(3df,3pd)/SMD(THF)) = -769.486191
Thermal correction to Enthalpy (wb97xd/6-311+G(d,p)/SMD(THF)) = 0.290789
Imaginary frequency: 94.97i

-1 1

C	-2.37706100	-1.81886900	0.95791500
C	-0.84458200	-1.93353200	1.14556800
C	-0.75531600	0.95248600	0.81427700
C	-2.25013100	0.76245900	0.76514700
C	-2.76750300	-0.56282400	0.18437900
H	-0.41203400	-1.89882300	0.11008700
H	-2.41969600	-0.65020400	-0.84753700
H	-2.82593400	-1.81300700	1.96108100
H	-2.67182300	1.57657600	0.16205700
H	-2.63722300	0.87621100	1.78203600
H	-3.86143500	-0.49320200	0.13773000
H	-2.77765000	-2.69151700	0.42502800
O	-0.37114500	-0.93407200	1.92578300
C	-0.50456800	-3.33525200	1.66600500
C	-0.03564600	-3.50825300	2.96631600
C	-0.66581800	-4.47025600	0.86535800
C	0.25328800	-4.77834900	3.46202900
H	0.10442500	-2.61835500	3.57090000
C	-0.37739400	-5.74044300	1.35181500
H	-1.01651300	-4.35469600	-0.15747200
C	0.08258600	-5.90069700	2.65796600
H	0.61757400	-4.89188900	4.47881300
H	-0.50597500	-6.60784400	0.71141700
H	0.31051800	-6.89047700	3.04029300
H	-0.36538400	1.27704600	1.76842200
C	0.09353000	1.08920300	-0.24845800
C	-0.23461100	0.96739200	-1.64854400
H	1.13695900	1.30037800	-0.04115300
O	0.89178600	1.05033200	-2.41548200
O	-1.33057900	0.85200800	-2.17370200
C	0.69765100	0.99810200	-3.82237600
H	0.07375700	1.82621000	-4.16858100
H	1.69134400	1.07758500	-4.26332400
H	0.23564400	0.05485200	-4.12448500

Validation of the computational method and the use of enthalpy in computed selectivities

Considering that both modes of activation result in kinetically-controlled cyclisation, transition states leading to the THP products were required in order to decipher the origin of stereoinduction. We started the transition state location using ωB97X-D density functional in conjunction with the 6-311+G(d,p) basis-set. After experimenting different approaches towards locating the transition states, the required transition states were obtained. It is important to point out that transition state could not be located in vacuum but with the use of solvation model. In addition, the obtained imaginary frequencies were rather low (freq(**2.1-trans**): 84.2i cm^{-1}, freq(**2.1-cis** TS): 69.6i cm^{-1}). This implies that the PES is rather flat around the transition states.[1] In addition to several factors, the flat curvature of the PES also results in severe uncertainty in the calculation of entropy. Moreover, we find that for the acid catalysed reactions, the computed selectivities using the Gibbs free energies are in qualitative agreement with those obtained experimentally. However, the computed selectivities for the base catalysed reactions using the Gibbs free energies results in selectivities opposite to that obtained experimentally. For these reasons, we use the enthalpy rather than Gibbs free energy to compute the selectvitities. It should also be noted that we are comparing intramolecular cyclizations featuring very little structural differences. Therefore, the net effect of entropy is posited in all the cases to be very similar.

To validate the applied theoretical method, we tested various density functionals to examine the functional-dependence of the predicted selectivity (Table 1). In line with the experimental results, all the tested functionals favour TS **2.1-trans** when using the electronic energy (E_0'), which was computed with the larger 6-311++G(3df,3pd) basis-set. This trend did not change when the electronic energies (E_0') were corrected with ZPEs adapted from ωB97X-D/6-311+G(d,p) calculations. Besides, the Gibbs free energies and the enthalpies were calculated by using the electronic energies obtained with different functionals (and using 6-311++G(3df,3pd) basis-set) and the corresponding thermal corrections adapted from ωB97X-D/6-311+G(d,p) calculations. With all the functionals, the trend in selectivity when using enthalpy of activation or energies of activation, remains qualitatively the same. But, the use of free-energies of activation results in qualitatively different selectivities. This once again confirms the perils of using free-energies with a large uncertainty involved in the computation of entropy.

In the case of the acid-catalysed cyclisation, the curvature of the potential energy surface at the TS is certainly more pronounced insomuch as the imaginary frequencies noticeably increased (freq(**1.1-cis**): 215.1i cm^{-1}, freq(**1.1-trans**): 233.5i cm^{-1}). We performed the same density functional test as with the TSs of the base-catalysed reaction (Table 2). All the tested functionals favour the TS **1.1-cis**, which results in the experimentally observed major isomer, with respect to all energy and thermodynamic terms listed in Table 2.

Overall, the similar results (same trend in selectivity when using enthalpies or energies) obtained with different density functions in Table 1 convinced us that the level of theory we used in the main text is adequate.

[1] Jensen, F. *Introduction to Computational Chemistry*, John Wiley & sons, **2017**.

Table 1 Base-catalysed cyclisation: single point energies computed with 6-311++G(3df,3pd) basis-set using various functionals and the respective Gibbs free energies and enthalpies calculated by the corrections adapted from ωB97X-D/6-311+G(d,p) calculations.

TS	*E*o'(THF) / Hartrees	d*E*o' (kcal)	*E*o'(THF)+ZPE / Hartrees	d(*E*o'+ZPE) (kcal)	*G* / Hartrees	d*G* (kcal)	*H* / Hartrees	d*H* (kcal)
	wB97XD/6-311++G(3df,3pd)		*Eo'(wB97XD/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(wB97XD/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(wB97XD/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-769.490349	**0.6**	-769.208783	**0.1**	-769.234656	**-0.3**	-769.200521	**0.3**
2.1-*trans*	-769.491359	**0.0**	-769.209014	**0.0**	-769.234208	**0.0**	-769.200958	**0.0**
	m062x/6-311++G(3df,3pd)		*Eo'(m062x/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(m062x/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(m062x/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-769.419641	**1.0**	-769.138075	**0.5**	-769.163948	**0.1**	-769.129813	**0.6**
2.1-*trans*	-769.421216	**0.0**	-769.138871	**0.0**	-769.164065	**0.0**	-769.130815	**0.0**
	m062x-D3/6-311++G(3df,3pd)		*Eo'(m062x-D3/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(m062x-D3/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(m062x-D3/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-769.421336	**1.1**	-769.139770	**0.6**	-769.165643	**0.1**	-769.131508	**0.7**
2.1-*trans*	-769.423020	**0.0**	-769.140675	**0.0**	-769.165869	**0.0**	-769.132619	**0.0**
	m06L/6-311++G(3df,3pd)		*Eo'(m06L/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(m06L/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(m06L/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-769.638117	**0.8**	-769.356551	**0.3**	-769.382424	**-0.1**	-769.348289	**0.4**
2.1-*trans*	-769.639368	**0.0**	-769.357023	**0.0**	-769.382217	**0.0**	-769.348967	**0.0**
	m06L-D3/6-311++G(3df,3pd)		*Eo'(m06L-D3/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(m06L-D3/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(m06L-D3/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-769.640045	**0.9**	-769.358479	**0.4**	-769.384352	**-0.1**	-769.350217	**0.5**
2.1-*trans*	-769.641420	**0.0**	-769.359075	**0.0**	-769.384269	**0.0**	-769.351019	**0.0**
	m052x/6-311++G(3df,3pd)		*Eo'(m052xL/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(m052x/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(m052x/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-769.659089	**0.9**	-769.377523	**0.4**	-769.403396	**-0.1**	-769.369261	**0.5**
2.1-*trans*	-769.660465	**0.0**	-769.378120	**0.0**	-769.403314	**0.0**	-769.370064	**0.0**
	m052x-D3/6-311++G(3df,3pd)		*Eo'(m052x-D3/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(m052x-D3/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(m052x-D3/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-769.662536	**1.0**	-769.380970	**0.5**	-769.406843	**0.1**	-769.372708	**0.6**
2.1-*trans*	-769.664130	**0.0**	-769.381785	**0.0**	-769.406979	**0.0**	-769.373729	**0.0**
	b3lyp-D3BJ/6-311++G(3df,3pd)		*Eo'(b3lyp-D3BJ/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(b3lyp-D3BJ/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(b3lyp-D3BJ/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-769.818186	**0.5**	-769.536620	**0.0**	-769.562493	**-0.4**	-769.528358	**0.1**
2.1-*trans*	-769.818970	**0.0**	-769.536625	**0.0**	-769.561819	**0.0**	-769.528569	**0.0**
	b2lyp-D3/6-311++G(3df,3pd)		*Eo'(b2lyp-D3/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(b2lyp-D3/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(b2lyp-D3/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-768.148492	**-0.1**	-767.866926	**-0.6**	-767.892799	**-1.0**	-767.858664	**-0.4**
2.1-*trans*	-768.148365	**0.0**	-767.866020	**0.0**	-767.891214	**0.0**	-767.857964	**0.0**
	B97D/6-311++G(3df,3pd)		*Eo'(B97D/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(B97D/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(B97D/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-769.266603	**0.5**	-768.985037	**0.0**	-769.010910	**-0.4**	-768.976775	**0.1**
2.1-*trans*	-769.267396	**0.0**	-768.985051	**0.0**	-769.010245	**0.0**	-768.976995	**0.0**
	B97D-D3/6-311++G(3df,3pd)		*Eo'(B97D-D3/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(B97D-D3/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(B97D-D3/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-769.219695	**0.4**	-768.938129	**-0.1**	-768.964002	**-0.5**	-768.929867	**0.0**
2.1-*trans*	-769.220312	**0.0**	-768.937967	**0.0**	-768.963161	**0.0**	-768.929911	**0.0**
	TPSSTPSS-D3BJ/6-311++G(3df,3pd)		*Eo'(TPSSTPSS-D3BJ/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(TPSSTPSS-D3BJ/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(TPSSTPSS-D3BJ/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-769.912385	**0.8**	-769.630819	**0.3**	-769.656692	**-0.1**	-769.622557	**0.4**
2.1-*trans*	-769.913671	**0.0**	-769.631326	**0.0**	-769.656520	**0.0**	-769.623270	**0.0**
	TPSSTPSS-D3/6-311++G(3df,3pd)		*Eo'(TPSSTPSS-D3/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(TPSSTPSS-D3/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(TPSSTPSS-D3/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-769.891442	**0.6**	-769.609876	**0.2**	-769.635749	**-0.3**	-769.601614	**0.3**
2.1-*trans*	-769.892472	**0.0**	-769.610127	**0.0**	-769.635321	**0.0**	-769.602071	**0.0**
	PBE1PBE-D3BJ/6-311++G(3df,3pd)		*Eo'(PBE1PBE-D3BJ/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(PBE1PBE-D3BJ/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(PBE1PBE-D3BJ/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-768.875746	**0.6**	-768.594180	**0.1**	-768.620053	**-0.3**	-768.585918	**0.2**
2.1-*trans*	-768.876660	**0.0**	-768.594315	**0.0**	-768.619509	**0.0**	-768.586259	**0.0**
	PBE1PBE-D3/6-311++G(3df,3pd)		*Eo'(PBE1PBE-D3/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(PBE1PBE-D3/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(PBE1PBE-D3/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
2.1-*cis*	-768.862465	**0.5**	-768.580899	**0.0**	-768.606772	**-0.4**	-768.572637	**0.1**
2.1-*trans*	-768.863242	**0.0**	-768.580897	**0.0**	-768.606091	**0.0**	-768.572841	**0.0**

ZPE(2.1-*cis*)= 0.281488; ZPE(2.1-*trans*)= 0.282284
*G*corr(2.1-*cis*)= 0.255693; *G*corr(2.1-*trans*)= 0.257151
*H*corr(2.1-*cis*)= 0.289828; *H*corr(2.1-*trans*)= 0.290401

Table 2 Acid-catalysed cyclisation: single point energies computed with 6-311++G(3df,3pd) basis-set using various functionals and the respective Gibbs free energies and enthalpies calculated by the corrections adapted from ωB97X-D/6-311+G(d,p) calculations.

TS	*E*o'(MeOH) / Hartrees	d*E*o' (kcal)	*E*o'(THF)+ZPE / Hartrees	d(*E*o'+ZPE) (kcal)	*G* / Hartrees	d*G* (kcal)	*H* / Hartrees	d*H* (kcal)
	wB97XD/6-311++G(3df,3pd)		*Eo'(wB97XD/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(wB97XD/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(wB97XD/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
1.1-*cis*	-3460.527746	**-0.7**	-3460.178588	**-0.7**	-3460.229480	**-0.4**	-3460.158305	**-0.7**
1.1-*trans*	-3460.526603	**0.0**	-3460.177524	**0.0**	-3460.228866	**0.0**	-3460.157174	**0.0**
	m062x/6-311++G(3df,3pd)		*Eo'(m062x/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(m062x/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(m062x/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
1.1-*cis*	-3460.440766	**-0.8**	-3460.091608	**-0.7**	-3460.142500	**-0.4**	-3460.071325	**-0.7**
1.1-*trans*	-3460.439562	**0.0**	-3460.090483	**0.0**	-3460.141825	**0.0**	-3460.070133	**0.0**
	m062x-D3/6-311++G(3df,3pd)		*Eo'(m062x-D3/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(m062x-D3/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(m062x-D3/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
1.1-*cis*	-3460.443338	**-0.6**	-3460.094180	**-0.6**	-3460.145072	**-0.3**	-3460.073897	**-0.6**
1.1-*trans*	-3460.442379	**0.0**	-3460.093300	**0.0**	-3460.144642	**0.0**	-3460.072950	**0.0**
	m06L/6-311++G(3df,3pd)		*Eo'(m06L/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(m06L/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(m06L/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
1.1-*cis*	-3460.538354	**-0.7**	-3460.189196	**-0.7**	-3460.240088	**-0.4**	-3460.168913	**-0.7**
1.1-*trans*	-3460.537184	**0.0**	-3460.188105	**0.0**	-3460.239447	**0.0**	-3460.167755	**0.0**
	m06L-D3/6-311++G(3df,3pd)		*Eo'(m06L-D3/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(m06L-D3/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(m06L-D3/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
1.1-*cis*	-3460.541269	**-0.6**	-3460.192111	**-0.5**	-3460.243003	**-0.2**	-3460.171828	**-0.6**
1.1-*trans*	-3460.540374	**0.0**	-3460.191295	**0.0**	-3460.242637	**0.0**	-3460.170945	**0.0**
	m052x/6-311++G(3df,3pd)		*Eo'(m052xL/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(m052x/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(m052x/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
1.1-*cis*	-3460.637512	**-0.8**	-3460.288354	**-0.7**	-3460.339246	**-0.5**	-3460.268071	**-0.8**
1.1-*trans*	-3460.636247	**0.0**	-3460.287168	**0.0**	-3460.338510	**0.0**	-3460.266818	**0.0**
	m052x-D3/6-311++G(3df,3pd)		*Eo'(m052x-D3/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(m052x-D3/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(m052x-D3/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
1.1-*cis*	-3460.642658	**-0.5**	-3460.293500	**-0.5**	-3460.344392	**-0.2**	-3460.273217	**-0.5**
1.1-*trans*	-3460.641839	**0.0**	-3460.292760	**0.0**	-3460.344102	**0.0**	-3460.272410	**0.0**
	b3lyp-D3BJ/6-311++G(3df,3pd)		*Eo'(b3lyp-D3BJ/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(b3lyp-D3BJ/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(b3lyp-D3BJ/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
1.1-*cis*	-3460.892853	**-0.7**	-3460.543695	**-0.7**	-3460.594587	**-0.4**	-3460.523412	**-0.7**
1.1-*trans*	-3460.891676	**0.0**	-3460.542597	**0.0**	-3460.593939	**0.0**	-3460.522247	**0.0**
	B97D/6-311++G(3df,3pd)		*Eo'(B97D/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(B97D/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(B97D/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
1.1-*cis*	-3461.533861	**-0.5**	-3461.184703	**-0.5**	-3461.235595	**-0.2**	-3461.164420	**-0.5**
1.1-*trans*	-3461.533007	**0.0**	-3461.183928	**0.0**	-3461.235270	**0.0**	-3461.163578	**0.0**
	B97D-D3/6-311++G(3df,3pd)		*Eo'(B97D-D3/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(B97D-D3/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(B97D-D3/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
1.1-*cis*	-3461.463946	**-0.8**	-3461.114788	**-0.7**	-3461.165680	**-0.4**	-3461.094505	**-0.8**
1.1-*trans*	-3461.462720	**0.0**	-3461.113641	**0.0**	-3461.164983	**0.0**	-3461.093291	**0.0**
	TPSSTPSS-D3BJ/6-311++G(3df,3pd)		*Eo'(TPSSTPSS-D3BJ/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(TPSSTPSS-D3BJ/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(TPSSTPSS-D3BJ/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
1.1-*cis*	-3460.887087	**-0.5**	-3460.537929	**-0.4**	-3460.588821	**-0.1**	-3460.517646	**-0.5**
1.1-*trans*	-3460.886334	**0.0**	-3460.537255	**0.0**	-3460.588597	**0.0**	-3460.516905	**0.0**
	TPSSTPSS-D3/6-311++G(3df,3pd)		*Eo'(TPSSTPSS-D3/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(TPSSTPSS-D3/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(TPSSTPSS-D3/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
1.1-*cis*	-3460.854911	**-0.6**	-3460.505753	**-0.6**	-3460.556645	**-0.3**	-3460.485470	**-0.6**
1.1-*trans*	-3460.853952	**0.0**	-3460.504873	**0.0**	-3460.556215	**0.0**	-3460.484523	**0.0**
	PBE1PBE-D3BJ/6-311++G(3df,3pd)		*Eo'(PBE1PBE-D3BJ/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(PBE1PBE-D3BJ/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(PBE1PBE-D3BJ/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
1.1-*cis*	-3459.467653	**-0.8**	-3459.118495	**-0.7**	-3459.169387	**-0.4**	-3459.098212	**-0.8**
1.1-*trans*	-3459.466429	**0.0**	-3459.117350	**0.0**	-3459.168692	**0.0**	-3459.097000	**0.0**
	PBE1PBE-D3/6-311++G(3df,3pd)		*Eo'(PBE1PBE-D3/6-311++G(3df,3pd))+ZPE(wB97XD/6-311+G(d,p))*		*Eo'(PBE1PBE-D3/6-311++G(3df,3pd))+Gcorr(wB97XD/6-311+G(d,p))*		*Eo'(PBE1PBE-D3/6-311++G(3df,3pd))+Hcorr(wB97XD/6-311+G(d,p))*	
1.1-*cis*	-3459.446895	**-0.8**	-3459.097737	**-0.8**	-3459.148629	**-0.5**	-3459.077454	**-0.8**
1.1-*trans*	-3459.445555	**0.0**	-3459.096476	**0.0**	-3459.147818	**0.0**	-3459.076126	**0.0**

ZPE(1.1-*cis*)= 0.349158; ZPE(1.1-*trans*)= 0.349079
*G*corr(1.1-*cis*)= 0.298266; *G*corr(1.1-*trans*)= 0.297737
*H*corr(1.1-*cis*)=.0.369441; *H*corr(1.1-*trans*)= 0.369429

Definition of pyramidalization of β-carbon

In addition to the bond-forming distance, we quantified the earliness-lateness of the TSs by the degree of pyramidalization of β-carbon in the Michael-acceptor fragment. The pyramidalization was measured by using the dihedral angle of 1(γ-C)-2(α-C)-3(H)-4(β-C). This angle describes how much the β-carbon comes out of the plane determined by 1(γ-C), 2(α-C) and 3(H) atoms. The value of this angle adequately indicates whether β-carbon is reactant-like or closer to the state of the product. For graphical definition of pyramidalization of β-carbon see below (Figure 1).

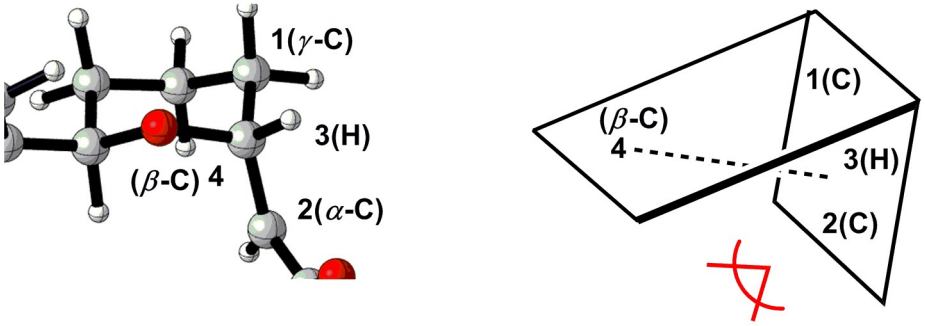

Figure 1 Measurement of pyramidalization angle: dihedral angle of 1(γ-C)-2(α-C)-3(H)-4(β-C)

Table 3 Pyramidalization angles.

Entity	*Angle (°)*
10a-alkoxide	0.0
TS **2.1-trans**	7.3
TS **2.1-cis**	9.2
enolate **2.2-trans**	34.5
enolate **2.2-cis**	35.7
10b-protonated	0.1
TS **1.1-trans**	16.1
TS **1.1-cis**	16.4
Enol **1.2-trans**	29.8
Enol **1.2-cis**	30.0